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Femtosecond laser ablation inductively coupled plasma mass spectrometry: achievements and remaining problems

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Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is considered to be one of the most versatile methods for trace elemental and isotopic analyses of solid material. Ever since the first feasibility studies initiated by A. Gray during the early 1980s [1], the performance characteristics of LA-ICP-MS have continuously been enhanced. Various operational parameters such as laser wavelength, pulse duration, fluence, carrier gas, and cell volume and/or geometry have been examined to specify conditions favorable for suppressing all effects, namely laser-, transport-, and ICP-induced ones, that result in inaccurate analyses [2–6]. The sum of these effects is commonly referred to as “elemental fractionation”. In addition, efforts have been made towards the development of alternative calibration [7] and ICP tuning strategies [8, 9] to further improve the quantification capabilities. As a result, LA-ICP-MS using deep UV nanosecond (ns) laser systems emitting at 193 nm has become a well-accepted technique for the “selective” trace element analysis of geological samples. The term “selective” refers to the persistent problem of quantifying elements such as Cd, Zn, Ag, or Pb with sufficient accuracy and precision. Apparently, these elements show a high degree of thermal volatility, low melting points, and partially different ionization potentials and are therefore extremely sensitive

to any changes of the LA and ICP conditions. Considering, for instance, the Pb- and U-specific isotope analysis of zircons, which is often used as a chronometer for geological events (geochronology), temporal drifts of the Pb/U ratio were found to restrict the accuracy [9, 10]. It should be emphasized that such fractionation-related inaccuracies can largely be avoided if matrix-matched standards are used for calibration. However, due to the lack of adequate reference materials, presently, only a few analytical problems can be solved on the basis of matrix matching.

In recent years, the aim of performing more comprehensive multi-element analyses including the abovementioned category of elements and increasing standards of precision and accuracy for a growing spectrum of matrices has required a permanent optimization of the instrumentation and analytical procedures as well as the development of strategies to suppress elemental fractionation. In this context, the utilization of ultra-short, i.e., femtosecond (fs) laser pulses probably represents the most promising instrumental advancement enabling the production of ultra-fine aerosol particles from a wide variety of samples, whose compositions exactly comply with that of the bulk material and, thus, allowing one to perform analyses which are less affected by elemental fractionation. In contrast to this, the design and operational characteristics of the ICP as a source of aerosol vaporization, atomization, and ionization have been nearly unchanged even though recent findings indicate that the present configuration does not generally fulfil the requirements for the analysis of laser-produced aerosols. This article reports on the prospects of fs-LA as a way to improve the quantification capabilities of LA-ICP-MS using non-matrix-matched calibration. It also addresses some of the remaining problems related to ICP-induced elemental fractionation which affect the overall accuracy of analysis.

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Elemental fractionation

Since the early 1990s, a series of authors (see, e.g., Refs. [2–6]) have reported on non-representative and temporally drifting elemental ratios commonly defined over two sequential parts of the acquired ICP-MS signal. Both phenomena—equally named elemental fractionation—represent the limiting factors that all analyses based on non-matrix-matched calibration are subject to. The examination of these effects has been considered as a crucial issue due to their obvious complexity involving laser-, transport-, and ICP-induced elemental fractionation. Among these, the role of laser-induced fractionation has lately attracted particular interest, since it was found to pre-define and, thus, to boost transport- and ICP-induced effects. The following example illustrates common practice of data treatment and the principal difficulties underlying any interpretation of LA-ICP-MS results in terms of fractionation.

Due to the lack of adequate reference materials, analyses performed by LA-ICP-MS often demand the utilization of non-matrix-matched standards for calibration and internal standardization in order to correct for varying, matrix-dependent ablation rates. The mean elemental ratios derived from this procedure can either exceed, reflect, or fall below the values that correspond to the actual bulk composition depending on the LA protocol and the acquisition period taken for analysis. Timing and width of this period is parameter-dependent and therefore based on empirical knowledge, since the relative contribution of each fractionation source—denoted as F_{laser} , $F_{\text{transport}}$, and F_{ICP} —during the ablation process cannot be predicted on a quantitative basis. As already suggested above, F_{laser} , $F_{\text{transport}}$, and F_{ICP} are correlated, implying that the overall fractionation is multiplicative in nature, i.e.,

$$\left. \frac{R_{\text{el. a}}}{R_{\text{el. b}}} \right|_{\text{exp.}} = \underbrace{F_{\text{laser}} \cdot F_{\text{transport}} \cdot F_{\text{ICP}}}_{:=F_{\text{tot.}}} \times \left. \frac{R_{\text{el. a}}}{R_{\text{el. b}}} \right|_{\text{theor.}} \quad (1)$$

Here, $R_{\text{el.}}(\text{exp.})$ and $R_{\text{el.}}(\text{theor.})$ denote the measured and expected elemental responses, respectively. Subscripts a and b refer to the elements analyzed.

Apparently, numerous combinations of Eq. (1) exist that result in the correct elemental ratio and there is no possibility of judging if the system is really fractionation-free within the acquisition period, i.e., F_{laser} , $F_{\text{transport}}$, and F_{ICP} equal unity, or if the individual sources simply compensate each other in a way such that only the overall fractionation index $F_{\text{tot.}}$ equals unity. From an analytical point of view, any combination resulting in $F_{\text{tot.}}=1$ would be acceptable provided that $F_{\text{tot.}}$ of the standard material also equals unity. Unfortunately, experimental conditions that allow for fractionation-free analyses in the former sense are dependent on the matrix and all parameters that affect the ablation process as well as the operational conditions of the ICP.

Of course, this line of arguments also applies to the marginal cases of small acquisition periods or stationary elemental ratios. It needs, however, to be stressed that stationary elemental ratios, i.e., the absence of temporal drifts, do *not* necessarily imply accurate analyses. For instance, raster-mode LA of homogeneous material results in constant elemental ratios which often depart from the actual bulk composition due to incomplete dissociation of μ -sized particles inside the ICP. On the other hand, the presence of temporal changes during the analysis of non-matrix-matched materials can yield correct elemental concentrations even if $F_{\text{tot.}}$ of the sample and standard material are not equal to one but merely identical. This rare situation occurs when the fractionation properties between calibration standard and sample to be analyzed are coincidentally equal or are adjusted to be the same via proper tuning of LA and ICP conditions.

The concept of stoichiometric sampling

According to the literature, UV-ns-LA-ICP-MS using non-matrix-matched calibration and internal standardization has successfully been applied to the analyses of various silicate glasses and minerals [11–14]. For metals and semiconductors, however, quantification by non-matrix-matched calibration turned out to be problematic, since strong heat diffusion into the target results in material re-distribution during the ablation process. As a consequence, the total composition of aerosols formed by ns-LA can considerably deviate from the bulk value, especially if intensively fractionating matrices such as metal alloys are analyzed [15, 16]. In order to restrain these effects, the laser pulse duration needs to fall below the material-specific thermal relaxation time.¹ For metals, which represent the most critical class of material in terms of zone heating, thermal relaxation takes place on a time-scale of few hundred fs. Reducing the pulse duration down to this region has, therefore, been suggested to improve the ablation characteristics and to get closer to the ideal concept of matrix-independent, “stoichiometric” LA [17].

Over the last five years, the performance characteristics of fs-LA as a method to create “stoichiometric” aerosols has been explored in several studies ranging from the compositional analysis of collected aerosol particles to ICP-MS- and optical emission spectrometry (OES)-based analyses. For instance, metallic as well as dielectric aerosol particles produced by NIR-fs-LA of brass and silicate glass were classified by low-pressure impaction and analyzed using total reflection X-ray fluorescence (TXRF). It could be demonstrated that the application of NIR-fs pulses permits

¹ Thermal relaxation refers to the time it takes to transfer the pulse energy absorbed by free electrons to the lattice ions.

Table 1 Dependency of PSDs and ACs on wavelength, fluence, and type of carrier gas for aerosols produced by ns-LA and fs-LA. The number of crosses specify the degree of correlation, i.e., + indicates no or minor dependency, ++ moderate dependency, and +++ strong

dependency. A rating for LA of organic matter cannot be given so far due to missing data. Assuming the conductivity and optical properties to be the most important parameters for LA, however, this category is supposed to behave similarly to non-conducting materials

	(Semi-)conducting PSD / AC	Non-conducting PSD / AC	Organic matter PSD / AC
Ns-LA			
Laser wavelength	+++ ↓ / ++ ↓ [23, 24]	+++ ↓ / + ↓ [21, 22, 25]	-/- ^a
Laser fluence	+++ ↓ / ++ ↑ [18, 23, 24]	-/- ^a	-/- ^a
Type of carrier gas	+++ ↓ / ++ ↓ [18, 24, 26]	+++ ↓ / + ↓ [21, 22, 25]	-/- ^a
Fs-LA			
Laser wavelength	+ ↔ / + ↔ [18, 27]	+ ↓ / + ↓ [19, 27]	-/- ^a
Laser fluence	++ ↓ / + ↓ [18]	++ ↑ / + ↑ [19]	-/- ^a
Type of carrier gas	+ ↔ / + ↔ [18]	+ ↔ / + ↔ [19]	-/- ^a

↓ decreasing wavelength, fluence, and atomic mass (carrier gas)

↑ increasing wavelength, fluence, and atomic mass (carrier gas)

↔ no significant influence reported yet

^aNo data available yet

one to create aerosols mainly consisting of particles within the so-called mesoscopic size range (ca. 10 nm up to 100 nm) that can efficiently be transported over large distances and whose overall composition exactly comply with that of the bulk if the LA settings such as wavelength, fluence, and type of gas are “adequately” chosen [18, 19].²

Unfortunately, all LA settings that control the particle size distribution (PSD) and aerosol composition (AC) are intercorrelated and are, in addition, dependent on the material to be analyzed. Therefore, an exact specification of reference values valid for the production of stoichiometric aerosols for different matrices cannot seriously be given. An assessment of ns- and fs-LA addressing the influence of wavelength, fluence, and type of gas on PSD and AC of conducting and non-conducting matrices is given in Table 1. Here, crosses indicate the degree of correlation and arrows whether wavelength, fluence, and atomic mass of the carrier gas should be decreased, increased, or stay unchanged to improve PSDs and ACs for ICP-MS analysis. As can be seen, fs-LA is distinguished by an only minor influence of LA conditions, whereas ns-LA shows a comparatively strong dependence on all parameters considered. For more details, please refer to the literature quoted.

Analysis of laser-produced aerosols by ICP-MS

In fact, the implementation of fs-LA-ICP-MS has been proven favorable for the analysis of solid materials in terms

² According to Garcia et al. [20], the transport efficiency of such aerosols can be larger than 80–90%, independent of cell volume or extraction geometry chosen. Here, the term transport efficiency refers to the aerosol fraction that is released to the surroundings and does not take into account material re-deposited on the sample surface due to back-diffusion, splashing, or gravitational settling of larger particles.

of the suppression of elemental fractionation. Improvements of precision (RSD) and accuracy have been reported for the analyses of metals, glasses, and minerals. For instance, Russo and co-workers [28] found elemental fractionation during the analysis of silicate glasses by near-IR (NIR) fs-LA-ICP-MS to be less pronounced. Gonzalez et al. [29], furthermore, demonstrated the feasibility of non-matrix-matched calibration for several Zn-containing alloy standards by applying UV-fs-LA-ICP-MS. Differences between certified and measured concentrations of the order of 10–20% were reported, which were four times smaller than values found for UV-ns-LA-ICP-MS using equivalent experimental conditions. Recently, Bian et al. [30, 31] and Monza et al. [32] communicated three studies on “extreme” cases of non-matrix-matched calibration using metal and silicate glass standards. In addition, Horn et al. [33] reported on the absence of isotopic fractionation during the isotope ratio analysis of a variety of Fe-containing mineral phases. Measurements were carried out on the basis of deep UV-fs-LA at ca. 200 nm and multi collector (MC)-ICP-MS.

It needs to be stressed that the analysis of ns and fs laser-produced aerosols via ICP-MS/OES as investigated in Refs. [28–33] provides information about the overall fractionation F_{tot} only, unless pulse energy, fluence, etc. are set to values appropriate for suppressing laser- and transport-induced effects. *If so*, the overall fractionation index as defined via Eq. (1) simplifies to

$$\frac{R_{\text{el. a}}}{R_{\text{el. b}}}\bigg|_{\text{exp.}} = F_{\text{ICP}} \times \frac{R_{\text{el. a}}}{R_{\text{el. b}}}\bigg|_{\text{theor.}} \quad (2)$$

since compositional changes due to laser- and transport-induced effects can be disregarded, i.e., both F_{laser} and $F_{\text{transport}}$ equal unity. In other words, inaccuracies should only be determined by ICP-induced fractionation under

these conditions. Stoichiometric aerosols generated by either ns- or fs-LA can therefore be considered as an ideal probe to inspect fractionation phenomena originating from processes such as preferential diffusion, intense mass loading, or non-representative sampling inside the ICP.

Extensive studies on existence and intensity of such matrix effects using UV-ns- and fs-LA-ICP-MS of standard reference materials (SRMs) have already been performed. According to Krosiakova et al. [34] and Koch et al. [27], mass-load-dependent matrix effects during UV-ns- and UV-fs-LA can change elemental ratios by more than 30% for low melting point elements. In the scope of the latter study, e.g., changes of the $^{66}\text{Zn}/^{65}\text{Cu}$ and $^{208}\text{Pb}/^{238}\text{U}$ signal intensity ratios were examined. For this purpose, aerosols produced by UV-fs-LA of silicate glass (SRM NIST610) were supplied to the ICP both undiluted and diluted. The dilution ratio was chosen to vary from 0.01 up to 1, thus, covering two orders of magnitude. Corresponding results are shown in Fig. 1 and reveal the $^{66}\text{Zn}/^{65}\text{Cu}$ ratio to drift by more than 30%. In contrast, relative changes of $^{208}\text{Pb}/^{238}\text{U}$ ratio were less pronounced by a factor of approximately two, i.e., 15%, whereas elemental ratios of non-critical systems such as $^{238}\text{U}/^{232}\text{Th}$ or $^{139}\text{La}/^{175}\text{Lu}$ (not shown here) remained almost unaffected. The trend of data points shown in Fig. 1, in addition, suggests that $^{66}\text{Zn}/^{65}\text{Cu}$ and $^{208}\text{Pb}/^{238}\text{U}$ ratios follow a so-called logistic decay for increasing aerosol densities, i.e., they tend to converge to constant values after passing an intermediate range of stronger changes. For dilution ratios well below 0.05, $^{66}\text{Zn}/^{65}\text{Cu}$ and $^{208}\text{Pb}/^{238}\text{U}$ ratios also stabilize, indicating that the evaporation and ionization properties of the ICP become less sensitive to changes of the aerosol mass entrained. In this range, the elemental ratios therefore reflect conditions that prevail in an almost *undisturbed* plasma source. For smaller dilution factors the convergence of elemental ratios results from increased mass loading which, paradoxically, pushes the working range to the edge of another stationary regime. According to O'Connor et al. [35], shifting the working range to stationary conditions by applying even stronger, i.e., excessive, mass loading based on simultaneous liquid aspiration can help to perform more reliable analyses of laser-produced aerosols, albeit at the expense of an increased oxide formation rate and polyatomic interferences. Furthermore, the admixture of wet aerosols is supposed to reduce the instrumental sensitivity even though not explicitly stated in Ref. [29].

Conclusions and outlook

Taking into account all data published on NIR- and UV-fs-LA-ICP-MS, it appears obvious that the utilization of fs laser radiation allows one to carry out analyses with a wider

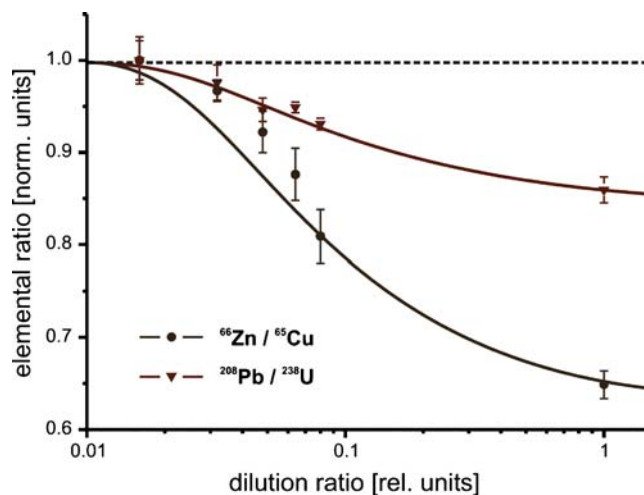


Fig. 1 Average $^{66}\text{Zn}/^{65}\text{Cu}$ and $^{208}\text{Pb}/^{238}\text{U}$ ratios acquired in UV-fs-LA-ICP-MS at ca. 265 nm by applying different dilution ratios from 0.01 to 1. The *dashed line* is representative for all elemental ratios that are not affected by varying aerosol masses as a result of similar thermodynamic properties and ionization potentials

range of matrices (including metals, alloys, oxides, silicates, etc.), which are less susceptible to laser-induced elemental fractionation compared to UV-ns-LA at 193 nm. However, it has also been shown that ICP-induced effects cannot generally be neglected, especially if high precision and accuracy are required (e.g., in Pb/U geochronology). Recent studies indicate that minor variations of an already small flow of material (ca. ng/s) inside the ICP may result in inaccurate quantification due to mass-load-induced matrix effects, even if the composition of the aerosol exactly corresponds to the sample material. Increased mass loading was found to particularly affect the analysis of elements whose volatility and first ionization potential significantly depart from that of the internal standard. Therefore, future investigations should aim to investigate

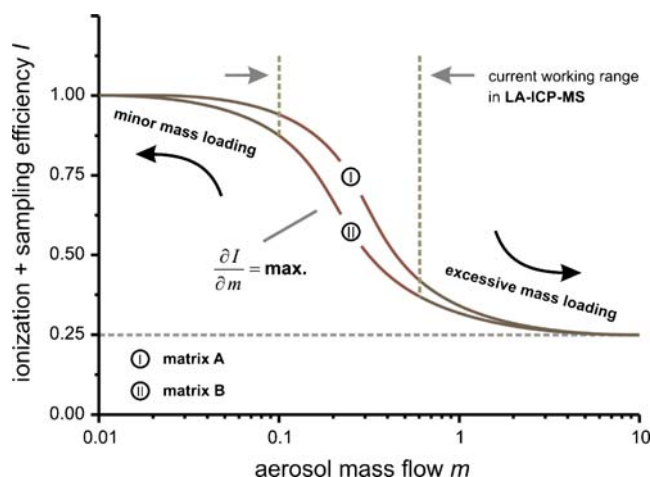


Fig. 2 Schematic representation of the influence of matrix and aerosol mass flow on the element-specific ionization efficiency of the ICP. *Vertical dashed lines* indicate the current working range of LA-ICP-MS

such processes unless the plasma source can be operated in a range that is not influenced by mass-loading-dependent ionization and sampling efficiencies. As illustrated in Fig. 2, pushing the working range of LA-ICP-MS to stationary conditions by either minor or excessive mass loading based on low-energy LA, aerosol dilution, or supplementary entrainment of aspirated liquids, respectively, could offer an option to circumvent this problem. However, the development of an alternative type of ICP (or maybe the re-invention of “old-fashioned” torch designs used before the Fassel torch became the generally accepted standard) that better meets the requirements of LA-ICP-MS would be desirable, but seems to be unlikely, at least in the near future. Meanwhile, an improvement in sensitivity of today’s available ICP-MS instrumentation represents the most promising strategy to overcome some of the limitations discussed.

There is increasing interest in fs-LA, but more comparative measurements concerning ns- and fs-LA will be necessary to finally assess its analytical capability. This is especially important for laboratories not dealing with the wide range of matrices that can be analyzed by LA-ICP-MS. As already shown in the past, a comparison of, e.g., different laser wavelengths, namely NIR, VIS, UV, without specific knowledge of the individual task is difficult to accomplish due to the complexity of all parameters involved. A meaningful comparison of ns- and fs-LA should, in addition, always address the mass transported to the ICP, as suggested above. Considering this, it might be possible that fs-LA will not significantly improve precision and accuracy for certain matrices such as oxides or silicates simply because the ablation process might be of lower importance in comparison to the mass carried to the ICP. These studies will, moreover, remain incomplete as long as non-homogenized laser radiation is used for fs-LA. Although the present generation of fs laser systems already provide a high degree of stability in terms of pulse duration, energy, etc., beam homogenizations still turn out to be difficult, since most of the concepts applicable are associated with a substantial energy loss and pulse stretching, in particular, with respect to frequency-converted, i.e., VIS or UV radiation. In contrast, state-of-the-art, UV-ns-LA systems already utilize well-homogenized laser radiation.

The acceptance of fs-LA as a sampling tool for ICP-MS analyses will, furthermore, depend on economic as well as practical aspects involving purchase price and ease-of-use of corresponding laser systems. One therefore needs to carefully evaluate what applications presently justify such an investment. Nevertheless, middle- and long-term perspectives seem to be quite promising, since the general interest in fs laser systems is constantly growing. Thus,

price cuttings and technological developments are expected to proceed in the same manner as for ns lasers.

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